Self - assembly of HgTe nanoparticles into nanostars using single stranded DNA

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Abstract

Self-assembly of structurally tunned nearly monodispersed HgTe - ssDNA nanostars of average size 1.4 nm have been achieved by manipulating HgTe nanoparticles using single stranded (ss) DNA under galvanostatic condition. The nanostars are linked with one another by ssDNA of length 0.35 nm. Whereas, HgTe nanoparticles without ssDNA complexation show a polycrystalline character with size in the range 4 - 7 nm. Room temperature photoluminescence (PL) of HgTe - ssDNA nanostars have yielded a single narrow PL at 548.4 nm of width 8 nm that corroborates to the nearly monodispersity of the nanostars and predicts the lateral exciton transfer. On the other hand, polydispersed HgTe nanoparticles exhibit free- and bound- exciton dominated luminescence in their PL spectrum.

Self-assembly of semiconductor particles and clusters in the nanoscale has become increasingly important in nanoscale science and technology for their novel properties derived from their size quantization[1–4] and surface effects[4,5]. Assembly of these nanostructures by conventional technique have yielded polydispersity and have encountered difficulties

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for the evaluation of their optical properties and even limited to their nanoscale device applications[6,7]. Thus, a bottom-up approach like wet chemistry or electrochemistry can be employed to synthesize nanostructured semiconductors with a good control over the size which is uncommon at this point of time. Assembly of such nanoparticles by sequence selective DNA could be a good strategy to achieve monodispersity and ordered nanoparticles. DNA is an important constitutent of the biological system consisting of nitrogenous bases like Purine (Guanine, G and Adenine, A) and Pyrimidine (Cytosine, C and Thyamine, T), deoxyribose sugar and phosphate group as an unit block. These are dictated by a network of specific hydrogen bonding interaction involving purine and pyrimidine bases with base to base separation as 3.4 A^o. Because of the presence of phosphate group, the backbone is negatively charged, giving polyelectrolyte (charges of same sign bound to a specific site of a polymer) nature to it. An interesting property associated with DNA molecule is it's elctrostatic interaction with positively charged ions, cations[8,9] in the solution analogous to the biological systems relevent to the DNA within a cell[10]. In particular, to organize DNA in chromatin (in eukariotic cells), nature utilize proteins having large positive charges histones and can form a stable bead-on-a- string nekless structure. Hence, it should be possible that such electrostatic interaction can self-assemble the nanocrystals under an electric bias onto a conducting substrate. In the present work we describe a new and simple strategy to synthesize mercury telluride (HgTe) - single stranded (ss) DNA nanostars taking above interaction of ssDNA into account and show the emergence of different structure, morphology and optical properties in comparision to HgTe nanoparticles without ssDNA. The unique optical properties involving lateral inter-nanostar exciton transfer as a result of self - assembling of nanoparticles in nanostar using ssDNA is being demonstrated by the photoluminescence measurement.

Although different approaches to assemble nanoparticle - DNA complex have been described in the literature[11–14], most of them have concentrated on colloidal particles (metallic nanoparticles) aggregation process based on light scattering and transmission

electron micrograph studies. None of them have considered the structural and/or photoluminescence (PL) aspects where the later is more pertinant to biosensor/identifying genetic disorder applications. For biosensors, one should have a very narrow PL line width which would be possible only from monodispersed nanocrystal semiconductors. Such an attempt has not been explored so far. In our approach, we have taken commercially available ssDNA $5\acute{}GCAAGCGGTGAACCAGTTGTG3\acute{}$ of 7.5 nm length with 21 base. $Hg^{2+}(0.014M)$ and $Te^{4+}(0.026M)$ were made available from their respective salt solutions. The electrolytic bath containing ssDNA, Hg^{2+} and Te^{4+} ions had pH = 0.6 at 278 K. The electrodes were indium tin oxide (ITO) coated conducting glass - cathode and Platinum - anode. Electrodeposition under stirring condition was carried out at 1.5 mA/cm^2 cathodic current for 2 minute. Although at 278 K, the ssDNA can form hairpin structure, in the stirring environment, there is always a restoring force acting on the ssDNA. Hence, for a guide to the eye, it has been represented by a coiling structure as shown in Fig. 1. Short chain ssDNA was choosen to avoid unwanted breaking of the chain during stirring and to get finite and separated HgTe - ssDNA complex nanostars. To check the stability of ssDNA in the working environment, optical absorption measurements were performed for 0.3 OD ssDNA in milipore water at pH= 0.6 and 278 K temperature. No appreciable change in absorption spectrum was noticed which confirms it's stability. In order to show superiority of our approach, we have also grown HgTe nanoparticles without ssDNA complexation keeping the deposition parameters same as described above. Our approach to synthesize HgTe - ssDNA complex nanostars is schematically outlined in Fig. 1. In step (1), the ssDNA is in the solution containing Hg^{2+} and Te^{4+} ions under continuous stirring environment. The negative potential due to charge distribution in ${PO_4}^{2-}$ group of ssDNA is largely compensated by the positive potential due to counter ions (positively charged) and condensation of counter ions start taking place with non- specific binding governed mainly by coulomb attraction. By that the ssDNA experiences an increase in entropy due to charge inversion[15] and starts wrapping around counter ions (in this case Hg^{2+} and Te^{4+}) to satisfy the charge neutrality condition as shown in step (2). In step (3), upon

impression of a current/potential between two electrodes, the ssDNA bases (G and A) are oxidized due to low oxidation potential[16]. As a result, partial charges are developed near G and A which generate a complex electric field whose distribution in the solution is given by $xA + yB = z(A + B)$ where A $\rightarrow$ Purine, B$\rightarrow$ Pyrimidine, $x = x_1 + x_2$ and $y = y_1 + y_2$, x_1 and x_2 are the total partial positive and negative charge developed near A and y_1 and y_2 are the total partial positive and negative charge developed near B where z is the total partial charge developed near the ssDNA bases. The coulomb interaction between the charges play an important role both in the formation of the structures and in transport processes. Thus, the Hg^{2+} and Te^{4+} ions are wrapped by the ssDNA after a charge inversion process which results in the generation of excess positive charge and form a complex with ssDNA in a random fashion. Upon impression of an electric field between the two electrodes the Hg^{2+} & Te^{4+} - ssDNA complex is alligned and dragged towards the cathode. The wrapped Hg^{2+} and Te^{4+} ions now take the required number of electrons from the cathode and subsequently hybridize themselves to form HgTe - ssDNA complex nanostars on the cathode[17].

As there are small number of HgTe nanoparticles in the wrapped DNA molecule, one would expect the formation of single crystals HgTe - ssDNA complex. Fig. 2 shows the TEM micrograph and diffraction pattern (inset) of HgTe without ssDNA taken at 80 KeV electron beam energy. The size of HgTe crystallites are in the range of 4 - 7 nm and non-spherical. The electron diffraction patterns clearly depicts polycrystalinity with preferred orientation in the sample and has the cubic structure. On the other hand the TEM micrograph and diffraction pattern (inset) shown in Fig. 3 depicts the HgTe - ssDNA complex nanostars are organised in a finite order with uniform in their lateral size (1.4 nm) and nanostars are linked with one others by ssDNA of length around 0.35 nm, incidentally this is also roughly the base to base separation of ssDNA (3.4 A^o). Our ssDNA length is 7.5 nm and crystalline size is 1.4 nm. If we assume that the ssDNA makes two and half turns on each HgTe nanocrystals (because of charge inversion) then, in that

case, the ssDNA can entangle at best two HgTe nanoparticles and form the nanostars as observed from TEM micrograph. The rest 0.5 nm ssDNA may have linked to another crystal or form a tentacle. Fig. 3 inset shows the diffraction pattern of HgTe - ssDNA deposit. Surprisingly the feature shows monocrystal structure and has cubic phase. The present work clearly demonstrates a superior self-assembling process for the HgTe - DNA systems.

The HgTe nanoparticles without ssDNA have the size in the range 4-7 nm which is much less than the Bohr exciton radius (40 nm). So, a prominent strong quantum confinement effect (QCE) has been observed with these nanocrystals. Thus, if such nanoparticles are excited with high energy photons (say UV light), one would expect light emission[18] in the visible regime which can help in biosensor or electroluminescence device applications. Indeed, our HgTe nanoparticles emit yellow-orange light at room temperature when excited with UV radiation ($\lambda = 369$ nm). Fig. 4 (a) is the photoluminescence spectrum of HgTe nanoparticles which consists two peaks, P_1 and P_2 peaking at 579.5 nm and 588.3 nm with full width of half maxima (FWHM) as 35 nm and 26 nm respectively and it needs explanation. Since localization energy of the exciton is the energy difference between peaks P_1 and P_2 which is around 31 meV and energy corresponding to room temperature is 26 meV and are comparable hence, some of the excitons are thermally released from the bound state as free exciton. As a result the luminescence, P_1 corresponding to free exciton transition and the red shifted narrow band P_2 whose energy is less than P_1 can be ascribed to the bound exciton transition. The narrowness of bound-exciton PL is due to the large spatial overlapping of initial and final state wave functions resulting increased in oscillator strength and short lifetime than free-exciton PL. If one assumes the effective mass approximation (EMA) then the average size estimated from the band edge PL (average size is 5.14 nm) does not match with TEM measurement. Such a descripancy is attributed to the non-sphericity in the nanoparticle and the particle in a finite potential well. On the contrary, the HgTe - ssDNA nanostars PL spectrum shown in Fig. 4 (b) gives a very narrow single peak at 548.4 nm with FWHM as low as 8 nm. Origin of blue

shifted narrow PL band compared to Fig. 4 (a) can be understood using the following reasons: (i) localization of the excitons as a result of carrier confinement by the ssDNA boundary of the nanostars acting as a resonator[19,20], (ii) if the separation between two quantum dots (QD) is small enough than the exciton dimension, then transfer of exciton from one QD to another is possible through diffusion mechanism, as a result of which the excitons of different QDs are populated and undergo coherent radiative recombination resulting a very narrow PL band[21] . Since the nanostars are linked with each other by ssDNA of length 0.35 nm as observed from TEM measurement hence, interaction between self - assembled nanoparticles through diffusion mechanism have resulted population of excitons which ungergo coherent radiative recombination to yield such a narrow PL line width. Such a narrow single PL peak suggests a nice perfection in the HgTe - ssDNA complex nanostars and clear observation of lateral exciton transfer between self - assembled nanoparticles. Such a single sharp PL peak have tremendous application in biosensors by anchoring the same with the conjugate ssDNA of $\acute{5}GCAAGCGGTGAACCAGTTGTG\acute{3}$. A very narrow PL peak is a prerequisite for any biosensor application if one intends to use PL as an optical probe for biosensor applications. The nanostars may even lead to identification of genetic disorder.

In summary, the present work clearly demonstrate an approach to use DNA molecules for complexation of precursor cations(Hg^{2+} and Te^{4+}), followed by their transport to and electrochemical reduction on the cathode and synthesize a new class of HgTe - ssDNA complex nanostar hybrid structures. Such structures are easily controllable and have resulted narrow line width luminescence and structural properties that are far different than HgTe nanoparticles. The most important spectral evidence of lateral excitons transfer is observed from PL measurement as a result of self - assembling of the nanoparticles into nanostars by ssDNA which have resulted narrow PL line width and can be used as a material candidate for biosensor application.

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Figures caption

Fig. 1. Schematic representation of the mechanism taking place during synthesis of HgTe - ssDNA complex nanostars.

Fig. 2. TEM micrograph of HgTe nanoparticles, inset the diffraction pattern.

Fig. 3. TEM micrograph of HgTe - ssDNA complex nanostars, inset the diffraction pattern.

Fig. 4. PL spectrum of HgTe nanoparticles (a) and HgTe - ssDNA complex nanostars (b). Solid line is the gaussian fitted curve of the PL spectrum.

FIGURES

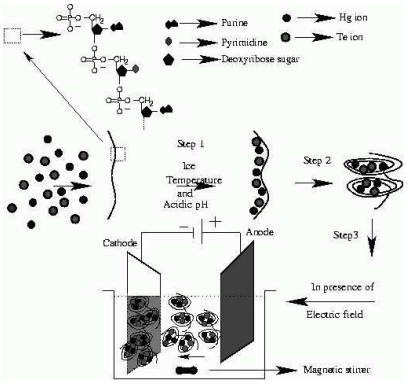

Fig. 1

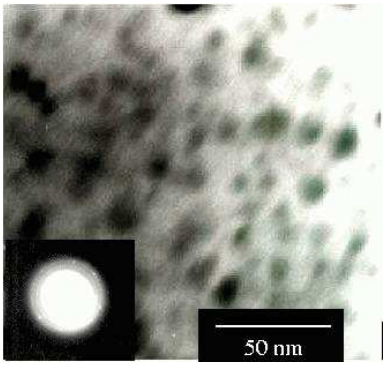

Fig. 2

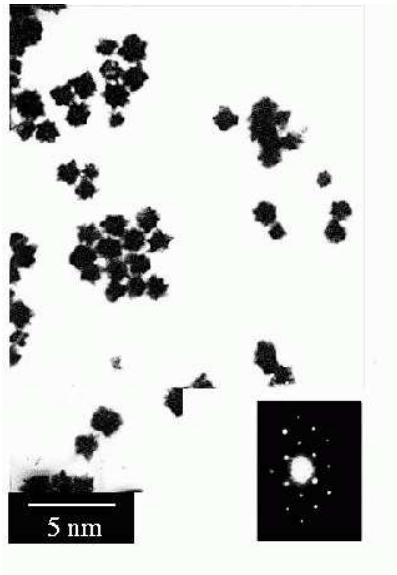

Fig. 3

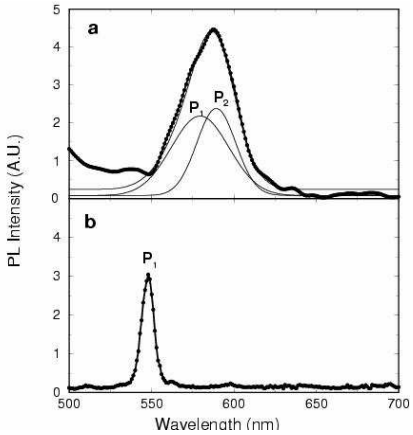

Fig. 4